

TITLE: CVD TECHNIQUES APPLIED TO ENERGY PROBLEMS

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Coatings by Chemical Vapor Deposition, (CVD), have proven to be useful in ICF research. In most cases, a few (1-50) carefully selected and characterized substrates are mixed with a few cubic centimeters of carrier particles and coated at reduced pressures in fluid-bed reactors. The procedures used to fabricate some specific targets will be discussed.

Another energy related program that is utilizing CVD techniques is the fabrication of high-temperature heat pipes<sup>(1)</sup>. Heat pipes have very high thermal conductance and the ability to handle very large heat fluxes.

In principle, a heat pipe consists of a tube closed at both ends and containing a working fluid that can exist as liquid and vapor at the working temperature. The liquid is vaporized at the heated end, travels through the tube and condenses at the other end to dump the heat. The liquid then returns to the evaporator. In a vertical pipe with the heat source at the bottom, gravity causes the liquid to flow down the tube wall to the evaporator. In other configurations it may be necessary to line a tube with a wick so that the liquid can return by capillary action.

Silicon carbide tubes are candidates for high temperature (1275-1375 K) heat pipes to be used in highly corrosive, oxidizing atmospheres because this material is relatively stable in such environments. However, sodium, the working fluid, attacks SiC and to prevent this attack, SiC tubes are being lined with CVD tungsten<sup>(2)</sup>.

The SiC tubes are subject to mechanical and thermal shock. In an attempt to circumvent this, extruded tubes of C/SiC were tested. Tubes made of this composite, after firing at 2375 K had better thermal shock resistance than CVD SiC, but were oxidized when heated in air<sup>(3)</sup>. So in addition to a CVD tungsten liner, the outer surfaces of the composite tubes were coated with CVD SiC from the hydrogen reduction of methyl trichlorsilane to prevent oxidation at the operating temperatures.

In a parallel effort to minimize shock fracture, CVD tungsten and CVD SiC coatings were reinforced with molybdenum screen. This was accomplished by wrapping cylindrical mandrels with one to three layers of 150 mesh molybdenum screen and coating the assembly to the desired thickness.

One problem involving heat pipes operating in outer space in the absence of gravitational effects is that a wick structure is required to return the condensed working fluid to the evaporator. One design for space operation requires cylindrical wicks, formed by wrapping a removable mandrel with 325 mesh molybdenum screen. The finest screen presently available is 150 mesh. Chemical Vapor Deposition molybdenum and tungsten are being used to close the porosity of the cylinders from 105  $\mu\text{m}$  down to 44  $\mu\text{m}$ .

## EXPERIMENTAL

### INERTIAL CONFINEMENT FUSION TARGETS

The current requirements for spherical ICF targets range in size from ~ 200- $\mu\text{m}$  diam to ~ 3-mm diam. The CVD coatings are usually formed on non-removable hollow glass microballoons (GMB's) or on removable solid metal

mandrels. In either case, only a few high quality substrates are available for a given experiment. To insure good coating conditions, the substrates are mixed with 2 to 10 cm<sup>3</sup> of carrier particles and are then coated in fluid beds. The carrier particles are screen-sized so that they can be separated from the substrates after coating.

Procedures and apparatus for coating small particles in fluid-beds were described in an earlier paper<sup>(4)</sup>. However, an improved coater design is shown in Fig. 1.

The important feature of this design is the co-axial orifice. Most of the fluidization occurs from the gas passing through the circular annulus. The reactant gas enters near the center of the bed, thus contacts the hot substrates and is depleted, to a large extent, before contacting the hot coater wall. This prevents, or minimizes the particles from sticking to the hot coater wall, which the very light GMB's tend to do.

Metal CVD coatings of current interest for ICF experiments include nickel, Mo<sub>2</sub>C and tungsten. Nickel and Mo<sub>2</sub>C\* are deposited from the pyrolysis of their carbonyls and tungsten is deposited from the hydrogen reduction of WF<sub>6</sub>. Glass microballoons are coated with nickel prior to tungsten coating to protect the glass from the HF formed in the reduction of WF<sub>6</sub>.

#### NICKEL COATINGS

CVD nickel coatings on ICF targets are made on various substrates in resistively heated pyrex fluid bed reactors. Nickel CVD coatings are currently being used primarily as thin (1/2 - 1 μm) layers either to protect substrates for chemical attack in subsequent CVD processes, or for activating non-conductive surfaces for subsequent electrochemical coatings<sup>(5)</sup>. Thicker coatings on small volumes (2 cm<sup>3</sup>) of GMB's are difficult to form because the nascent nickel surfaces are very cohesive and destroy the fluid-bed action.

#### TUNGSTEN COATINGS

Tungsten coated ICF targets are made on various substrates in inductively heated fluid-bed graphite reactors from WF<sub>6</sub> and hydrogen at ~ 700 K, and at reduced pressures of 10-100 torr.

One set of ICF targets was made by diffusing a 50/50 mixture of deuterium/tritium gases at 750 K through 35-μm-thick CVD tungsten shells. The shells were formed on 1.1-mm-diam hollow metal spheres (Solacels obtained from the Solar Division, International Harvester Corp., San Diego, CA) that were carefully selected and characterized as to size, shape, wall thickness and wall uniformity, i.e., concentricity. To retain their identity each sphere was coated separately, suspended in a carrier bed of smaller Solacels. The original requirement was for 100-μm-thick tungsten, but it proved to be impractical to diffusion fill through thick CVD tungsten, so after filling through the ~ 35-μm shells, the targets were electrolytically plated with gold to form 100-μm-thick shells.

\* In reference 4, it was stated that molybdenum metal was deposited from the pyrolysis of Mo(CO)<sub>6</sub>. Subsequent x-ray diffraction and ion probe analysis proved the coating formed at 625 K to be Mo<sub>2</sub>C.

Diffusion filling through any practical thickness of tungsten is a slow process and significant quantities of tritium and deuterium are lost in, and through the hot pressure vessel during the filling process. Also, the quality of commercial hollow metal spheres is not adequate to satisfy the target designers. To circumvent both of these problems, a procedure was developed to gas-fill through a hole in a tungsten shell, and to simultaneously plug the hole to trap the gas in the target.

The tungsten shells were formed on precision solid molybdenum mandrels (Industrial Tectonic Inc., Ann Arbor, MI), and the mandrels were removed by chemical leaching through a 0.076-mm-diam hole drilled in the shell. After mandrel removal, a plug machined from a braze material that wets tungsten (68 wt% silver, 27 wt% copper, 5 wt% palladium) was inserted in the hole, and the assembly was pressured and heated to  $\sim 1125$  K to melt the plug and trap the gas<sup>(6)</sup>. The filling-plugging apparatus is shown in Fig. 2. One target, filled at 5000 psi (34 MPa) with deuterium contained 4506 psi (31.06 MPa), and one target filled at 10000 psi (68.9 MPa) of deuterium burst on cool down, indicating that the plug had sealed the hole. A metallographic section of typical thick-wall-CVD tungsten on a solid mandrel is shown in Fig. 3, and a section through a plugged hole is shown in Fig. 4. In practice, the debris on the outer surface, shown in this figure, would be removed by lapping. It should be possible to improve this process by using laser energy to melt the plug.

In contrast to the thick-wall-tungsten shells, very thin shells were made using the same technique. Shells  $\sim 1$   $\mu$ m thick were successfully made. A present requirement is for 1/2- $\mu$ m-thick-wall shells.

In an attempt to increase the bursting strength of thick shells, 1-mm-diam TZM mandrels were coated with 25 wt% rhenium - 75 wt% tungsten from a mixture of the metal fluorides. The mandrels were supported in a fluid-bed graphite coater. A metallographic section of a rhenium-tungsten shell is shown in Fig. 5. The coating consists of light and dark bands, with the light bands progressively less frequent. Ion probe analysis of this specimen indicated that the coating became progressively less rich in rhenium. Holman and Huegel<sup>(7)</sup> explained similar phenomenon in that the deposition rate of rhenium from a mixture of  $\text{ReF}_6$ - $\text{WF}_6$  is supply limited in contrast to the rate for tungsten which is temperature limited. Early in this run, the mandrels were suspended near the coater orifice in a rhenium rich environment and as the run progressed, the carrier particles became heavier and more supportive, causing the mandrels to ride higher in the bed, in a rhenium poor environment. This effect was visually apparent during the run. These shells have not been pressure tested.

#### TUNGSTEN SHELLS ON GLASS

Requirements for high-Z microballoons were met by depositing tungsten from  $\text{WF}_6$  onto nickel coated GMB's. Approximately 1- $\mu$ m-thick nickel, from  $\text{Ni}(\text{CO})_4$  was adequate to protect the thin-wall GMB's from HF attack. This procedure produced smoother coatings than coatings on bare GMB's from  $\text{W}(\text{CO})_6$ .

### DIMOLYBDENUM CARBIDE SHELLS

Dimolybdenum carbide coatings have proven to be quite useful in laser fusion target fabrication. They are strong, smooth, relatively free of nodules and can be diffusion filled with deuterium-tritium gases. Targets are typically coated with  $\text{Mo}_2\text{C}_3$  in an apparatus similar to the one shown in Fig. 1 by passing  $\sim 300^2 \text{ cm}^3/\text{m}$  of carrier gas (hydrogen or argon) through granular  $\text{Mo}(\text{CO})_6$  stored in the water-jacketed tube at 325 K to transport  $\text{Mo}(\text{CO})_6$  vapor into the fluid bed at 625 K. The system pressure is maintained at  $\sim 300$  torr. Using these conditions, the average partial pressure of  $\text{Mo}(\text{CO})_6$  during a run is 1-2 torr. These conditions result in low coating rates, about  $0.3 \mu\text{m}/\text{h}$ , and produce smooth, stress free coatings. These coatings are routinely made for a variety of ICF target requirements.

### COMPOSITE LASER FUSION TARGETS

In the proceeding section some uses of CVD processes to fabricate simple targets were discussed. The same procedures are being used to fabricate complex multi-shell targets composed of high, medium and low-Z and high, medium and low density layers. A description of one such target follows.

Glass microballoons, 200- $\mu\text{m}$  diam having 2-to-4- $\mu\text{m}$ -thick walls were diffusion filled with 25 atm (2.53 MPa) of deuterium-tritium. Approximately 200 of the filled GMB's were mixed with  $\sim 2 \text{ cm}^3$  of carrier GMB's, also  $\sim 200\text{-}\mu\text{m}$  diam. The mixed bed was then coated with  $5.5 \mu\text{m}$  of  $\text{Mo}_2\text{C}$ . After coating, the filled GMB's were separated from the carrier by an autoradiography technique<sup>(8)</sup>. In this process the GMB's were spread, one layer thick onto a fine screen grid in contact with a photographic film. The radiation from the filled GMB's exposed the film and after exposure and development, the film was used to locate the filled GMB's. They were then removed from the grid with a vacuum microprobe. The targets were then coated with 20- $\mu\text{m}$ -thick plastic using a low pressure plasma polymerization technique. In this procedure cyclooctatetraene vapor is fragmented in the plasma, forming active fragments which recombine and polymerize on the GMB's. Random motion of the particles was obtained using an electromechanical shaker. The targets were then coated with  $\sim 1\text{-}\mu\text{m}$ -thick CVD nickel to activate the plastic surfaces for depositing a 4- $\mu\text{m}$ -thick shell of electrolytic gold<sup>(5)</sup>. The last step in the target fabrication was to deposit another plastic layer  $\sim 50 \mu\text{m}$ -thick. A metallographic section of a practice target minus the outer plastic shell is shown in Fig. 6.

### CERAMIC HEAT PIPE

Both beta-phase SiC tubes formed on removable mandrels by CVD (Materials Technology, Dallas, TX.) and alpha-phase SiC tubes prepared by sintering (Carbonrondum Corp., Niagara Falls, NY) are being used. The apparatus used to coat an alpha-phase tube 19-mm i.d., 32-mm o.d. x 610-mm long is shown in Fig. 7. A co-axial gas delivery tube was designed to provide uniform delivery of  $\text{WF}_6$  through each of the 0.102-mm-diam holes spaced at 100-mm intervals when the inlet pressure was  $\sim 300$  torr and the system pressure was  $\sim 10$  torr<sup>(4)</sup>. The SiC tube was rotated slowly about the delivery tube to overcome effects due to off-axis position of the tubes. The distribution of tungsten obtained in the first run is shown as a pictorial

representation in Fig. 8. Wall thicknesses were obtained from full scale x-radiographs and are probably accurate to  $\pm 20\%$ . The thin deposit near the closed end was apparently due to a plugged hole in the delivery tubes. Variations in wall thickness above some minimum thickness necessary to protect the SiC are acceptable since this should not affect the wicking action of the liner. Metallography of the tungsten, shown in Fig. 9 indicates small cross section columnar crystals, normal to the substrate.

The optimum structure would probably consist of  $\sim 0.25$  mm of fine-equiaxed grains for maximum protection with the exposed surface being dendritic or pyramidal to enhance wicking. There is some evidence that thermal cycling of heat pipes has caused coarse grained tungsten to rupture and thereby expose the SiC to attack by the working fluid; small grained structures may minimize this. It may be possible to restrict the growth to fine grains by periodic doping and/or interrupting the coating process. If reliable liners can be formed in 610-mm-long pipes, the process will be scaled to coat pipes up to 2-m long.

Since heat pipes are subject to both thermal and mechanical shock, it is desirable to improve the resistance to fracture of both SiC and tungsten. Chemical vapor deposition has been used to infiltrate structures for various uses, including improved fracture resistance (10)(11). As a preliminary step to determine the feasibility of reinforcing heat pipes and liners, 150 mesh molybdenum screens were embedded by CVD in tungsten and in SiC. In the tungsten tests, the screens were wrapped around CVD tungsten cylinders that were formed on thin-wall molybdenum tubes. The tungsten coatings then were continued to embed the screens. Metallographic cross-sections show the results in Fig. 10 and 11. Grain growth is columnar, normal to the substrate surfaces. The unetched areas are sections perpendicular to grains that are normal to the circumferential wires of the screen. Voids probably formed when cells in the screen were occluded before the cells were filled with tungsten. A longitudinal crack about 20-mm long formed in one test piece after coating. As shown in Fig. 11, the wire screen may have stopped the crack from propagating through the cylinder wall.

A screen wrapped around a cylindrical tube of C/SiC was embedded in SiC formed from the hydrogen reduction of trichloromethylsilane at 1575 K and 75-90 torr using a 3:1 ratio of hydrogen to silane. The 12-mm-o.d., 100-mm-long tube was mounted vertically in a 25-mm-o.d. quartz tube, and was heated inductively. The gases were metered through mass flow meters into the bottom of the quartz tube. Coating rates were about 0.17 mm/h. As shown in Fig. 12, the screen appears to be firmly encased in the SiC. X-ray analysis of the SiC deposited in this study indicated beta-phase with a 111 preferred orientation with no excess silicon. Emission Spectroscopy Chemical Analysis confirmed the absence of excess silicon and indicated a composition of about 65 wt% silicon and 35 wt% carbon. A scanning electron micrograph of a SiC surface indicates a columnar structure in Fig. 13. The characterization of this material is consistent with that described by Chin, et al (12) deposited under similar conditions. A considerable amount of testing will be necessary to determine the effectiveness of wire reinforcing tungsten and SiC, but if it proves to be useful, the addition of screen would probably not complicate the CVD process.

An alternate method to fabricate a ceramic heat pipe is being developed by the Nuclear Fuels Section at Los Alamos. Rather than form the SiC tube by a CVD process, a composite of C/SiC is extruded as a tube and fired in argon at 2375 K. These extruded tubes resist thermal shock better than pure SiC, but at the present state of development are not as strong as pure SiC. Also, the free carbon in the structure is readily oxidized at elevated temperatures. Several of these tubes were lined with CVD tungsten and were coated with CVD SiC to protect the composite from sodium attack and from oxidation. An end view of a coated tube is shown in Fig. 14. The SiC shown in Fig. 12 was formed on a C/SiC composite tube. The results from these coatings indicate that CVD tungsten and SiC coatings are compatible with the composite material, but the coated composites have not been tested in an operating environment. If this process can be developed to form satisfactory heat pipes, it probably would be preferable to a pure CVD SiC process.

#### METAL HEAT PIPES

The preferred pore dimensions in the wick structure in one type of metal heat pipe is about 40  $\mu\text{m}$  (325 mesh screen). At present, the smallest molybdenum screen available is 150 mesh, with 105- $\mu\text{m}$  pores. Preliminary runs on 12-mm-diam x 100-mm-long cylinders formed of 150 or 100 mesh molybdenum screen indicates that CVD molybdenum can be used to close the structure to the desired porosity. The cylinders were hung in a vertical quartz tube, and were heated inductively via a graphite susceptor to 775 K. The gases,  $\text{MoF}_6$  + hydrogen were metered through mass flow meters into the bottom of the reactor. The system pressure was  $\sim 15$  torr. Results of one run on a 100 mesh screen are shown in Fig. 15. The relatively even closure and rough surface should make a satisfactory wick.

The designers of this heat pipe had hoped that in addition to reducing the porosity, the CVD process would also firmly bond the wires in overlapping layers of screen that were in contact. This did not occur: very little force was adequate to separate the coated layers. As shown in Fig. 10, the coatings grew as columnar grains normal to all surfaces and when grains from opposing surfaces came into contact, growth stopped and no bonding occurred.

This process will be scaled up to coat 12-mm-diam x 2-m-long cylinders. The cylinders will be formed of three layers of 150 mesh molybdenum screen. Obviously, some development work must be done to scale from 100 cm to 2 m.

#### CONCLUSIONS

Chemical vapor deposition techniques are being used and developed to coat a wide variety of devices ranging in size and shape from sub-millimeter diameter spheres to 2-m long cylinders. Coating thicknesses vary from sub-micron to a few millimeters. Most of the programs are energy related: Inertial Confinement Fusion, which may some day provide abundant and inexpensive energy and energy transfer devices to be used in such diverse programs as coal-gasification and reactors in outer space.



Most of the chemistry used in the CVD processes is well known, and in general presents no particular difficulty. The major problems are mechanical: how to fluidize a small number of very small, light particles that will not behave as a fluidized particle should and how to uniformly distribute the gases over long, small diameter cylinders, or in long, small, diameter bores. However, these problems usually can be overcome, and satisfactory, if not perfect results can be obtained. In many cases, CVD techniques are the only solution, especially where refractory metals and carbides are required.

#### ACKNOWLEDGMENTS

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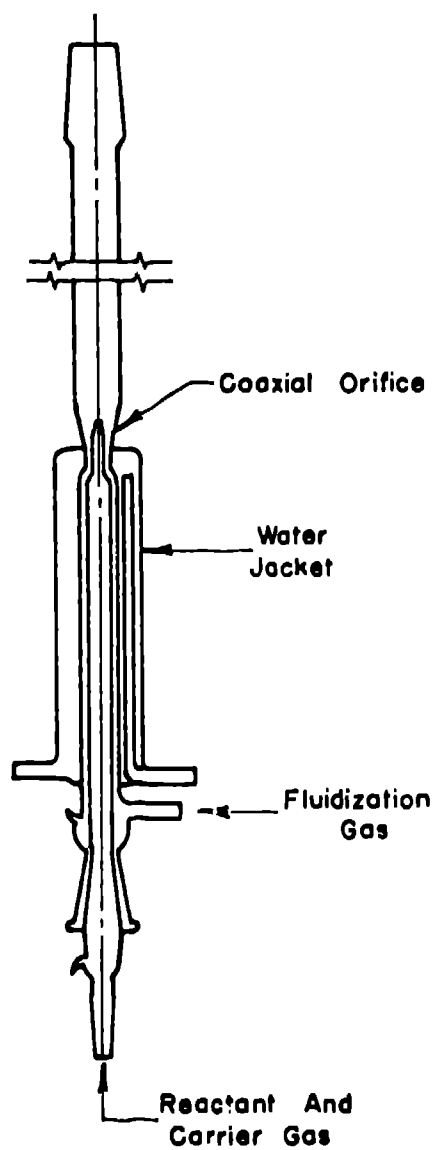


Fig. 1 Pyrex Fluid-Bed Cooler

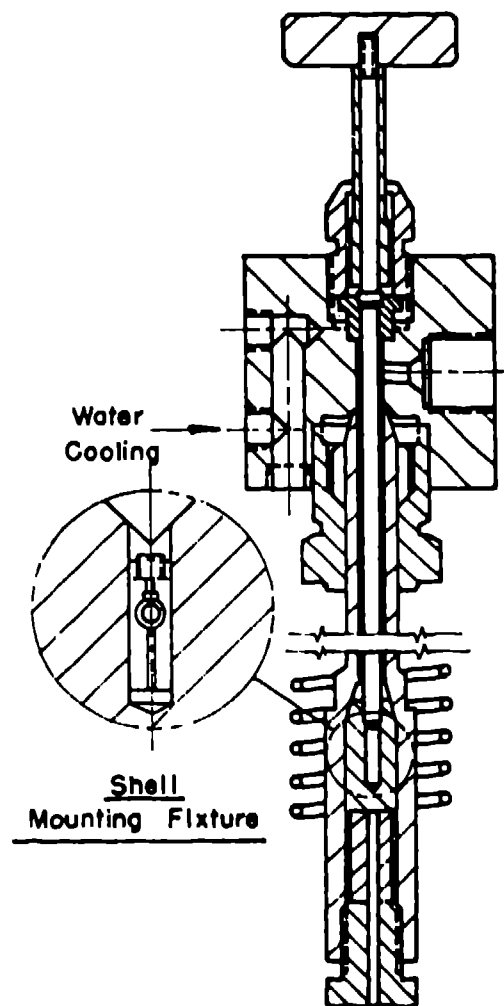


Fig. 2 Fill-Plug Apparatus

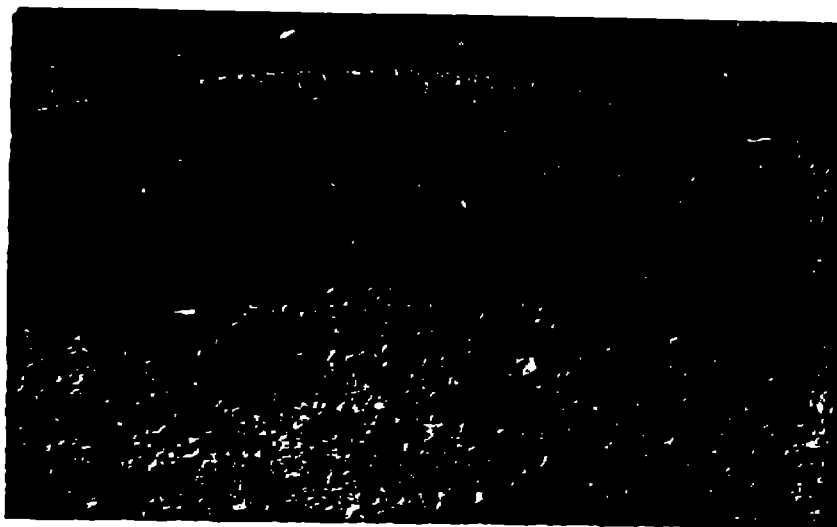


Fig. 3. CVD W on TZM 100  $\mu\text{m}$  Thick.



Fig. 4. Plugged 60  $\mu\text{m}$  Diam Hole in CVD W Shell 100  $\mu\text{m}$  Thick.

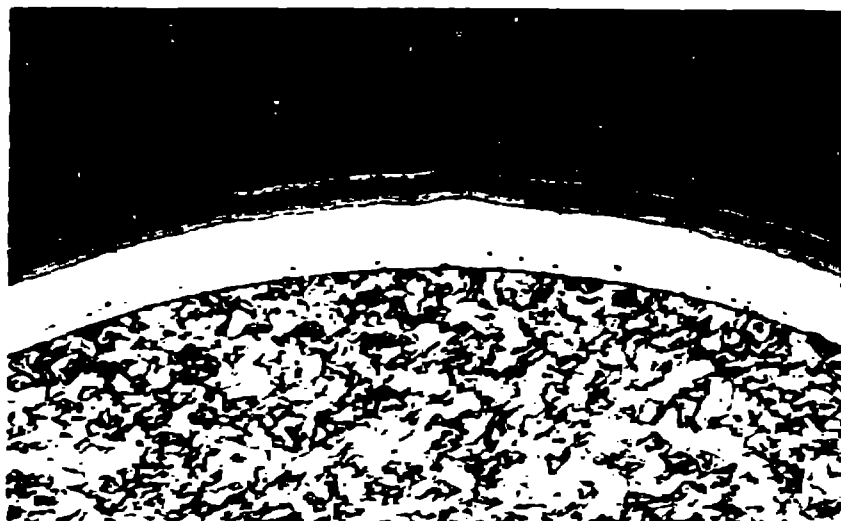


Fig. 5. CVD W/Re on TZM 89  $\mu\text{m}$  Thick.

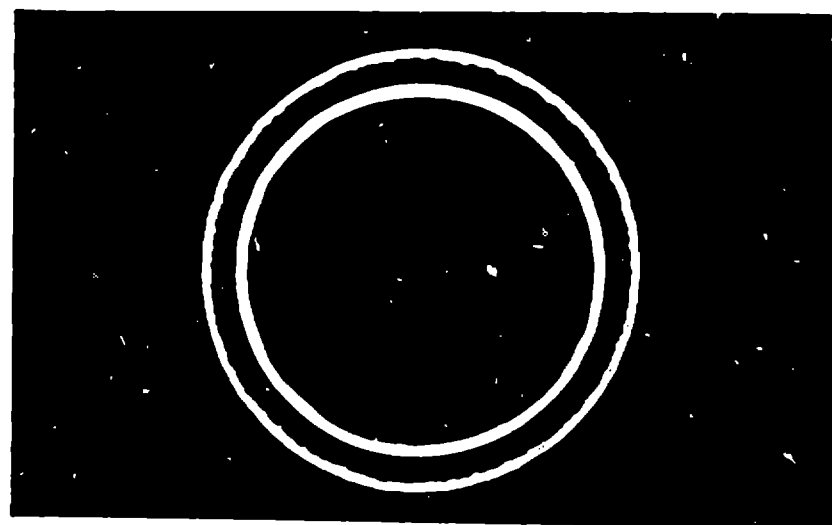


Fig. 6. Composite Laser Fusion Target;  
Glass +  $\text{Mo}_2\text{C}$  + Ni + Au 230  $\mu\text{m}$  o.d.

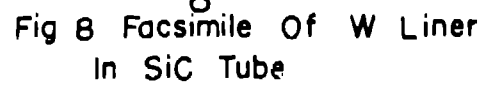




Fig. 9. CVD W Liner in SiC Tube; 55  $\mu\text{m}$  Thick



Fig. 10. Mo 150 Mesh Screen in CVD W  $\left| \text{---} 200\mu\text{m} \text{---} \right|$



Fig. 11. Mo 150 Mesh Screen in CVD W  $\left| \text{---} 200\mu\text{m} \text{---} \right|$



Fig. 12. Mo 150 Mesh Screen in CVD SiC 44  $\mu\text{m}$  Thick

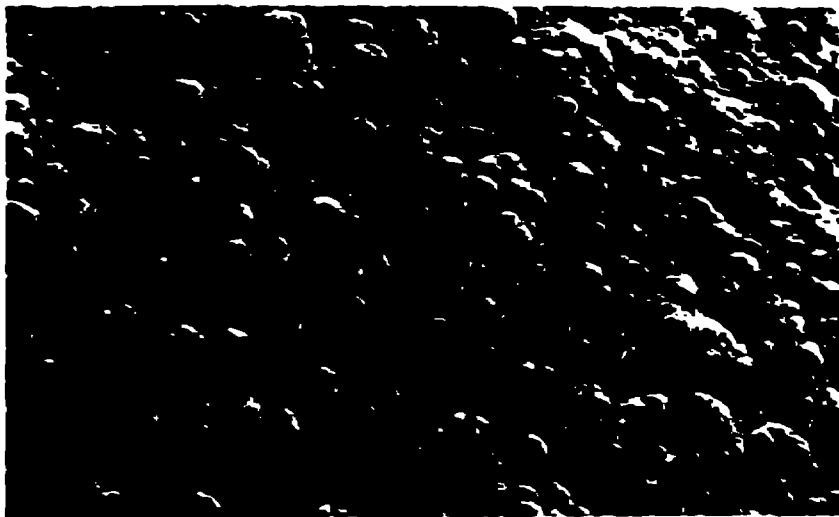


Fig. 13. SEM of CVD SiC Surface → 200 $\mu$ m ←

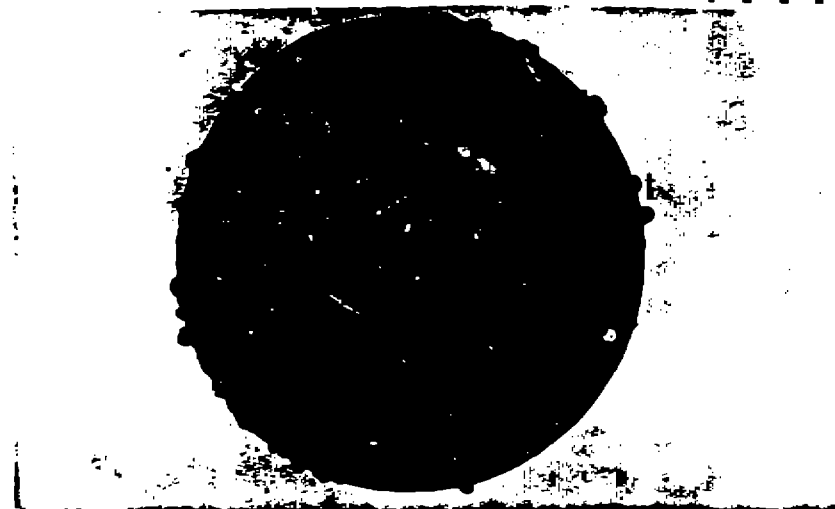


Fig. 14. Cross-Section of SiC/C Tube Liner and SiC Coating 13.0 mm o.d.



Fig. 15. CVD Mo on 100 Mesh Mo Screen → 200 $\mu$ m ←